

CHAPTER 2

THEORIES

2.1 Biomass

Biomass is organic material made from plants and animals. Biomass contains stored energy from the sun. Plants absorb the sun's energy in a process called photosynthesis, which is the reaction of carbon dioxide in the air, water and sunlight. When burned, the chemical energy in biomass is released as heat (U.S. Energy Information Administration). It can be converted into modern energy carriers such as gaseous, liquid fuels and electricity as a substitute for fossil fuels. Biomass fuels available for gasification include charcoal wood and agricultural residue.

2.2 Component of Biomass

The main components of any biomass material are cellulose, hemicellulose, lignin and small amounts of other extractives. These components are mainly considered for the understanding of decomposition mechanisms of woody and herbaceous biomass. It varies from species to species. Woody plants are a solid lignocellulosic material naturally produced in trees and some shrubs and are composed of 40-50% cellulose, 20-30% hemicellulose and 20-30% lignin (Tiwari and Ghasal, 2005). While herbaceous plants are generally non-woody species of vegetation. It is biennials or perennials and low lignin content.

Cellulose is the carbohydrate that is the principal constituent of wood and other biomass and forms the structural frame work of the wood cells. It forms the skeletal structure of the plant cell wall (Rowell, 2005).

Hemicelluloses are a group of polysaccharide polymers which are present in the cell walls of all plants. The hemicellulose component of the cell wall helps prevent infection, provides strength, and protects against other external agents (Rowell, 2005).

Lignin is highly complex, amorphous, three-dimensional polymer. It is like cellulose which the only elements involved is C, H, and O. Unlike cellulose which consists of macromolecules, lignin contains a high proportion of aromatic compounds (compounds

containing benzene rings). Lignin is generally found in the cell walls of certain biomass, especially woody species (Rowell, 2005).

Extractives are the organic components which can be removed by extraction with solvents without altering the cellulose/lignin structure of the wood. Extractives are often classified according to the type of solvent which can be used to extract them from the wood. Solvents include water, alcohol, benzene and ether. Extractives include tannins and other polyphenolics, coloring matter, essential oils, fats, resins, waxes, gums and starch (Donegan *et al.*).

2.3 Fuel Properties of Biomass

2.3.1 Moisture Content

Moisture in natural biomass material is composed of water in the cavity during growth and in the surface from humid air. The moisture content can be referred to on a wet basis, on a dry basis, and on a dry ash free basis. Normally, it is expressed on a wet basis which refers to the weight of water as a percentage of the total wet fuel weight. Biomass with high moisture content has a significant effect on its conversion efficiency and heating value. During biomass combustion, the generated heat required to evaporate the water. Not only loss of combustion efficiency but also transportation of moisture biomass is less efficiency (Klass,1998).

2.3.2 Volatile Matter Content

Volatile matter refers to the part of biomass that is released when the biomass is heated. During the heating process, the biomass decomposes into volatile gases and solid char. Biomass normally has a high volatile matter content (up to 80%), whereas coal has a low volatile matter content (less than 20%) (Quaak *et al.*, 1999).

2.3.3 Fixed Carbon Content

Fixed carbon is the amount of combustible material remaining in a sample after removal of moisture, volatile matter and ash. It is determined by subtracting the mass percentages of moisture, volatile matter, and ash from 100% (Klass,1998).

2.3.4 Ash Content

Ash content represents the inorganic residue which remains after the combustion of biomass. The ash content can be expressed on a wet, dry, or dry ash free basis. In general, the ash content is expressed on a dry basis. It consists mainly of silica, alumina, ferric oxide, lime, and some of magnesia. These compositions of the ash affect its behavior under the high temperatures of combustion and gasification. For example, melted ash may cause problems in reactor (Klass, 1998).

2.3.5 Elemental Composition

The elemental components of biomass are carbon (C), hydrogen (H), Oxygen (O), and small proportion of sulfur (S) and nitrogen (N). The percentages of C, H, O, S, and N are important for determining the amount of air for complete combustion or gasification. The elemental compositions can be used to calculate the higher heating value of biomass also (Klass, 1998).

2.4 The Fundamental of Gasification

Gasification is a thermochemical process in the presence of controlled O_2 (generally 35 percent of the amount of O_2 theoretically required for complete combustion or less). It converts a solid fuel or carbonaceous fuel, such as coal, petroleum, biofuel, or biomass, to a combustible or synthetic gas (e.g. H_2 , CO , CO_2 , CH_4). In general, gasification involves the reaction of carbon with gasification agents such as air, oxygen, steam etc. at 600-700°C or higher to produce a gaseous product that can be used to provide electric power and heat or as a raw material for synthesis of chemicals, liquid fuels, or other gaseous fuels (Armesto *et al.*, 2002; Klass, 1998).

2.4.1 Basic of Biomass Gasification

The chemical reaction of solid particles such as biomass is complicated because of their porous structure. The chemical reaction sequence for gasification can be explained below.

Devolatilization or Pyrolysis is the first step when heating up biomass particles. Devolatilization occurs already at low temperatures (350-800°C) parallel with the heating up of the biomass particles. A wide range of products are released through the decomposition of fuel, including tars, hydrocarbon liquids, and gases, including CH_4 , CO ,

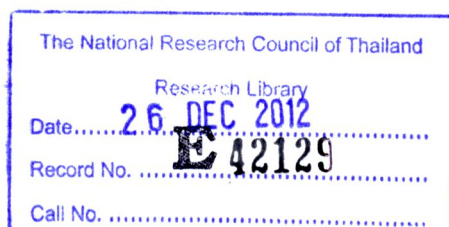
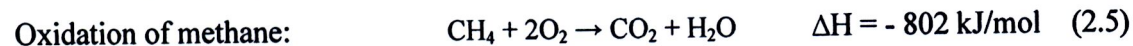
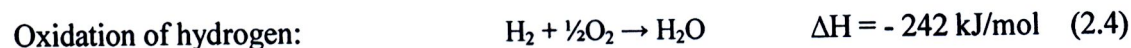
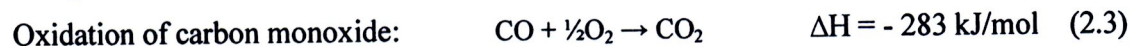
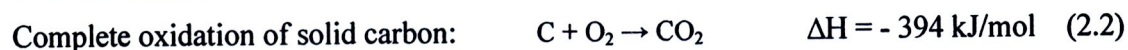
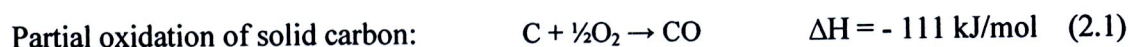
CO₂, H₂, H₂O, HCN, and so on. The rate of devolatilization depends on the rate of heating, the particle size, temperature, residence time and type of fuel.

Volatiles Combustion is the later step in which the products of the devolatilization step react with the oxidants surrounding the biomass particle. The volatile matter burns in a diffusion flame at the boundary between O₂ and unburned volatiles. The combustion rate is usually controlled by the diffusion of volatiles and O₂ at their interface. The extent to which the oxidant is completely or only partially depleted depends on the amount of volatiles produced.

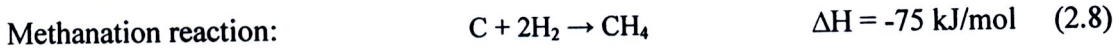
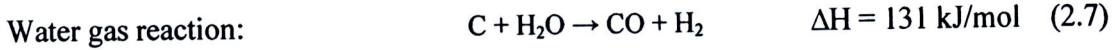
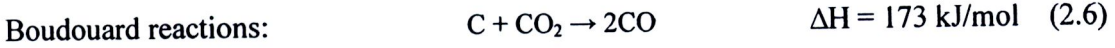
Char Gasification is the slowest reaction in the gasification process. The intrinsic chemical reactivity of the carbonaceous material is determined by the heterogeneous reaction, namely the water gas, the Boudouard, and the hydrogenation reactions. The rate of reaction for the water gas and the Boudouard reactions with char are comparable and are several orders of magnitude faster than the hydrogenation reaction (Basu, 2006; Higman and Burgt, 2003).

2.4.2 Gasification Reaction

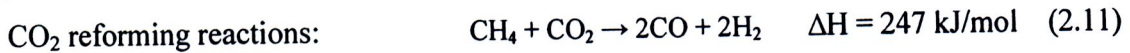
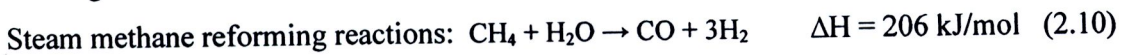
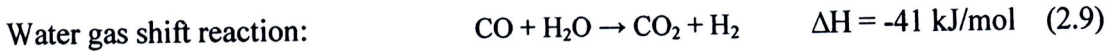
The gasification process requires heat to dry the moisture content in the upper most layers of the biomass in order to perform several endothermic reactions of devolatilization. During devolatilization, light volatile carbon (CH₄, CO, CO₂, H₂, H₂O), condensable organic compound (tars) and a solid residue (char: containing rich carbon) are released. Fixed carbon and ash are by-products from devolatilization which are not vaporized. The oxidation or combustion of char is the reaction taking place inside a gasifier, providing the heat required for the endothermic reactions. O₂ supplied to the gasifier reacts with the some part of char to form CO₂ and H₂O that are the following reactions (Basu, 2006; Kaewluan, 2009).



These gas products subsequently react with the char produced from devolatilization to form combustible gases by carbon heterogeneous reactions which are the Boudouard reactions, the water gas reaction and the methanation reaction. All of these reactions are desirable to determine a syngas composition (Higman and Burgt, 2003; Kaewluan, 2009).



In addition, homogeneous gas reactions also take place parallel to the heterogeneous reactions in the following ways (Basu, 2006; Kaewluan, 2009):



2.4.3 Gasification Technology

Gasification is the technology for extracting energy from biomass. Many kinds of biomass gasification processes have been developed for treating different materials for various purposes.

Single-Stage Gasifiers

The aim of a single-stage gasifier is to convert organic substances entirely in one reactor. Depending on the type of operation, different gasification agents are supplied. The most commonly used gasification technologies for single-stage processes are fixed bed, fluidized bed and entrained flow gasifier.

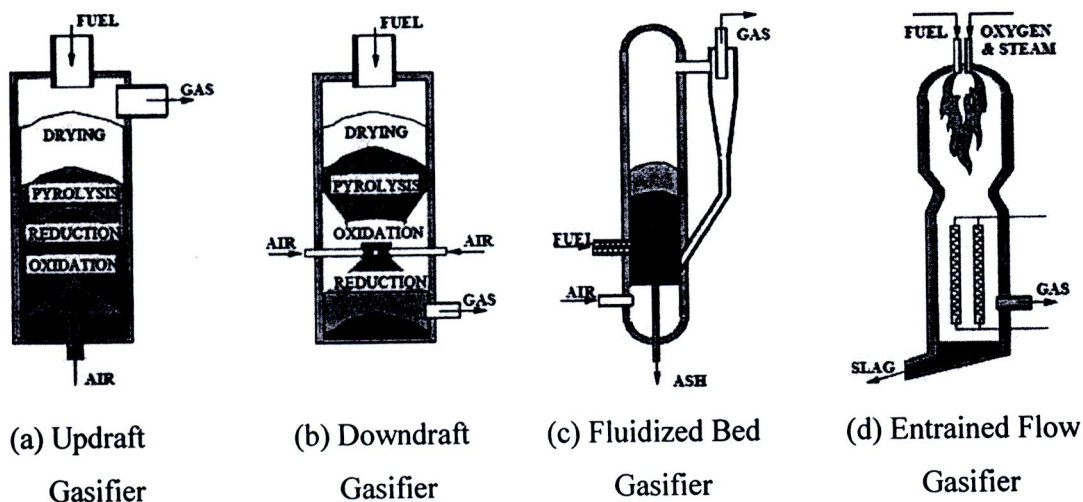


Figure 2.1 Gasifier types (Judex, 2010)

Fixed Bed Gasifiers

Fixed bed or moving bed gasifiers are often counter-current flow systems (Fig. 2.1a). The biomass is fed into the top of the reactor and moves downward. Air is taken in at the bottom and gas leaves at the top. This type achieves high efficiency because the hot gas passes through the entire fuel bed and leaves the gas producer at a low temperature. However the high amounts of tar and pyrolysis products occur because pyrolysis gas does not pass the combustion zone and therefore is not combusted (Phi, 1988; Quaak *et al.*, 1999). Another type of fixed beds is co-current gasifier (Fig. 2.1b). In a co-current fixed bed gasifier, the fuel and air move in the same direction. The main advantage of this type is gaseous product compose of low tar content. But the moisture content of the biomass must be less than 25 percent (on a wet basis) (Kaewluan, 2009; Quaak *et al.*, 1999).

Fluidized Bed Gasifiers

Fluidized bed gasifiers (Fig. 2.1c) allow more efficient gasification because fixed bed gasifiers are limited in the moisture content of the biomass that they can readily gasify. Fluidized bed gasifier can usually process higher moisture content fuels and various types of biomass (Henrich *et al.*, 2000).

An inert material such as sand is the fluidization medium. The biomass is fed into a suspended hot sand bed. A gas flow is introduced through the bottom of a bed of solid particles that will move upwards through the bed via the empty spaces between the particles. The bed of solid particles will behave as a fluid. Fuel particles mix quickly with the bed material, resulting in rapid pyrolysis and a relatively large amount of gaseous

product. As the fuel burns, the turbulence of the burning bed keeps the temperature stable (Phi, 1988).

The advantages of fluidized bed gasification are (Kaewluan, 2009):

- providing high rate of heat transfer between inert materials, fuels and gases
- a nearly uniform temperature distribution throughout the reactor
- low fuel content in the beds
- high carbon conversion efficiency

The disadvantages of fluidized bed gasification are:

- need power consumption for the compression of the gas stream
- high producer gas temperature

Entrained Flow Gasifiers

Entrained flow gasifiers (Fig. 2.1d) require pulverized fuels. The biomass particles are introduced into the steam/oxygen feed and gasified at a residence time of a few seconds. Gasifiers can be operated at lower temperature to maintain ash as a dry solid, or at temperature well above the ash fusion point in the slagging mode so that ash is removed as molten liquid. Their use for biomass gasification is rather limited, as it requires the fuel particles to be very fine (80-100 μm) (Basu, 2006; Hamel *et al.*, 2007).

However, none of the common gasifier types is perfectly suited for biomass fuel. The main reason is the high tar content because it blocks and fouls the equipment and creates high risk of reactor slagging, due to the low ash sintering temperature in the presence of much potassium. To improve the gasification process, the study of two-stage gasifiers concept is a good basis which the feed is considered, whereas amount of tars is reduced and reactor slagging by sintering ash is avoided.

Two-Stage Gasifiers

In general, gasification and combustion are always preceded by a pyrolysis step. The two-stage processes enhance process efficiency and product gas quality by the separating pyrolysis reactor prior to gasification.

In the first stage, the biomass is dried and pyrolysed in a fluidized bed of sand at temperatures below the ash softening temperature of about 600°C in an indirectly heated pyrolyser. The gasification agent can be added to sustain bed fluidization and to reduce tar

formation. The volatiles escape from the fuel at temperatures below 600°C, leaving solid char.

In the second stage is an autothermal gasification of the pyrolysis gas and the solid pyrolysis char at temperature above 800°C after partial oxidation with air or oxygen (Henrich *et al.*).

2.4.4 Two-Stage Gasifiers

The typical two-stage gasification system, shown in Figure 2.2, consists of five parts: feeding unit, pyrolysis unit, char gasifier, air preheating unit and gas cleaning unit. The system may also include an engine, gas analysis unit and a control system.

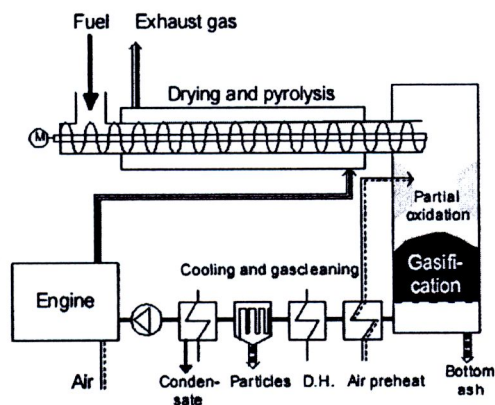


Figure 2.2 Typical schematic layout of a two-stage gasification system (Yi *et al.*, 1997)

Pyrolysis Unit - The pyrolysis unit may be a transport screw or fluidized bed with external heating (for typical two-stage gasification system, heated by exhaust gas from the engine). In the pyrolysis unit, the volatiles escape from the fuel at temperatures below 600°C, leaving solid coke. In the case of the fluidized bed, the pyrolysis char must be separated from the bed material prior to gasification.

Partial oxidation - At the end of the pyrolysis, the coke and the volatiles fall through the high temperature (1100 – 1300°C) partial oxidation zone directly into the gasification chamber. Adding preheated air in a turbulent swirl causes the partial oxidation of the volatiles. Due to high temperature, the tars in the pyrolysis gas are cracked.

Gasification - The char is gasified in the gasification reactor. H₂O and CO₂ from the partial oxidation act as gasification agents to convert the char into combustible gasses.

Gas cooling and cleaning - After coarse particle removal in a cyclone, the gas is cooled in a heat exchanger. Soot particles are removed in a bag house filter before the gas is cooled in a condensing cooler (Henrich *et al.* and Yi *et al.*, 1997)

2.5 Fluidization

A fluidized bed is established when the velocity through the reactor is high enough to lift the material which is in the reactor. The buoyancy of the material marks the transition from a fixed bed to a fluidized bed. This point is called minimum fluidization with the characteristic minimum fluidization velocity u_{mf} . Increasing the velocity leads to an expansion of the material until the grains are entrained. Before this point the bed is called bubbling. If the material is deliberately entrained and recirculated into the bed it is called circulating fluidized bed. Then the velocity in the reactor is higher than the terminal velocity u_t . A bubbling fluidized bed consists of two phases: a bubble phase which is considered particle free and a dense bed which is a mixture of gas and particles. It becomes clear that heterogeneous reactions like char gasification will take place in the dense phase, whereas homogeneous reactions can take place in both phases (Judex, 2010).

2.5.1 Bed Material

The bed material can be used as a heat carrier and can catalyze the gasification reaction. The bed material can be of various types. There are several important properties of the bed material which should be considered (Judex, 2010):

- reactivity (influence on the reaction mechanisms)
- density and size of the particles (responsible for the fluidization characteristic)
- specific heat (responsible for the temperature texture in the bed)

2.5.2 Minimum Fluidization Velocity

When the solid particles are fluidized, the fluidized bed behaves differently as velocity. The determination of the minimum fluidization velocity (U_{mf}) is an important parameter in the efficient operation of a fluidized bed system. There are 2 methods to determine U_{mf} which are: experiment and calculation.

U_{mf} from the experiment

Ambient air is applied to the reactor under the distributor plate to investigate the relationship between the pressure drop across the bed, ΔP , and superficial velocity. When the gas passed upwards through the fixed bed, ΔP increases with superficial velocity. The minimum fluidization velocity is the velocity which the pressure drop across the bed to be constant. A typical plot of the pressure drop versus the velocity is shown in Figure 2.3.

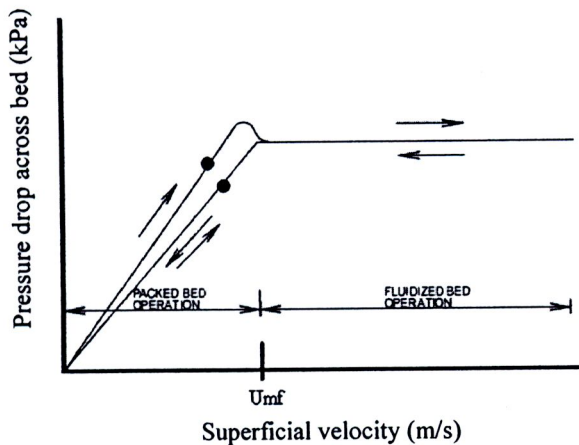


Figure 2.3 Relationship between pressure drop across the bed with fluid velocity (Chase)

U_{mf} from the calculation

U_{mf} can be calculated with the Ergun Equation as below:

$$1.75 \frac{1}{\phi \epsilon_{mf}^3} \text{Re}_{mf}^2 + 150 \frac{1 - \epsilon_{mf}}{\phi^2 \epsilon_{mf}^3} \text{Re}_{mf} = \text{Ar} \quad (2.12)$$

Here:
$$\text{Ar} = \frac{d_p^3 \rho_f (\rho_s - \rho_f) g}{\mu^2} \quad (2.13)$$

$$\text{Re}_{mf} = \frac{d_p U_{mf} \rho_f}{\mu} \quad (2.14)$$

(A) A small-sized particle bed ($\text{Re}_{mf} < 20$)

$$U_{mf} = \frac{\epsilon_{mf}^3 (\rho_s - \rho_f) (\phi d_p)^2 g}{(1 - \epsilon_{mf}) 150 \mu} \quad (2.15)$$

(B) A big-sized particle bed ($\text{Re}_{mf} > 1000$)

$$U_{mf}^2 = \frac{(\rho_s - \rho_f) \phi_s d_p g \epsilon_{mf}^3}{1.75 \rho_f} \quad (2.16)$$

Where:

ϵ_{mf} = voidage at minimum fluidization

μ = fluid viscosity (kg/m-s)

ρ_f = gas density (kg/m³)

ρ_s = particle density (kg/m³)

d_p = diameter of particle (m)

g = acceleration of gravity, 9.81 m²/s (m²/s)

ϕ_s = sphericity factor

2.5.3 Terminal Velocity

For applications, the terminal velocity (U_t) of a particle needs to be determined. The value of terminal velocity can be calculated in the different region of Reynold's number as below:

Stokes law,
$$\frac{d_p U_t \rho_f}{\mu} = \frac{Ar}{18} \quad \text{for} \quad Re < 0.4 \quad (2.19)$$

Intermediate law,
$$\frac{d_p U_t \rho_f}{\mu} = \left[\frac{Ar}{7.5} \right]^{0.666} \quad \text{for} \quad 0.4 < Re < 500 \quad (2.20)$$

Newton's law,
$$\frac{d_p U_t \rho_f}{\mu} = \left[\frac{Ar}{0.33} \right]^{0.5} \quad \text{for} \quad Re > 500 \quad (2.21)$$

Here:
$$Ar = \frac{d_p^3 \rho_f (\rho_s - \rho_f) g}{\mu^2} \quad (2.22)$$

Where:

d_p = diameter of particle (kg/m³)

ρ_f = gas density (kg/m³)

ρ_s = particle density (kg/m³)

g = acceleration of gravity, 9.81 (m²/s)

μ = fluid viscosity (kg/m-s)